

Monosubstitution at 4-Position of 2,7-Carbazolyene Expands Structural Design and Fundamental Properties of D- π -A Copolymers for Organic Photovoltaic Cells.

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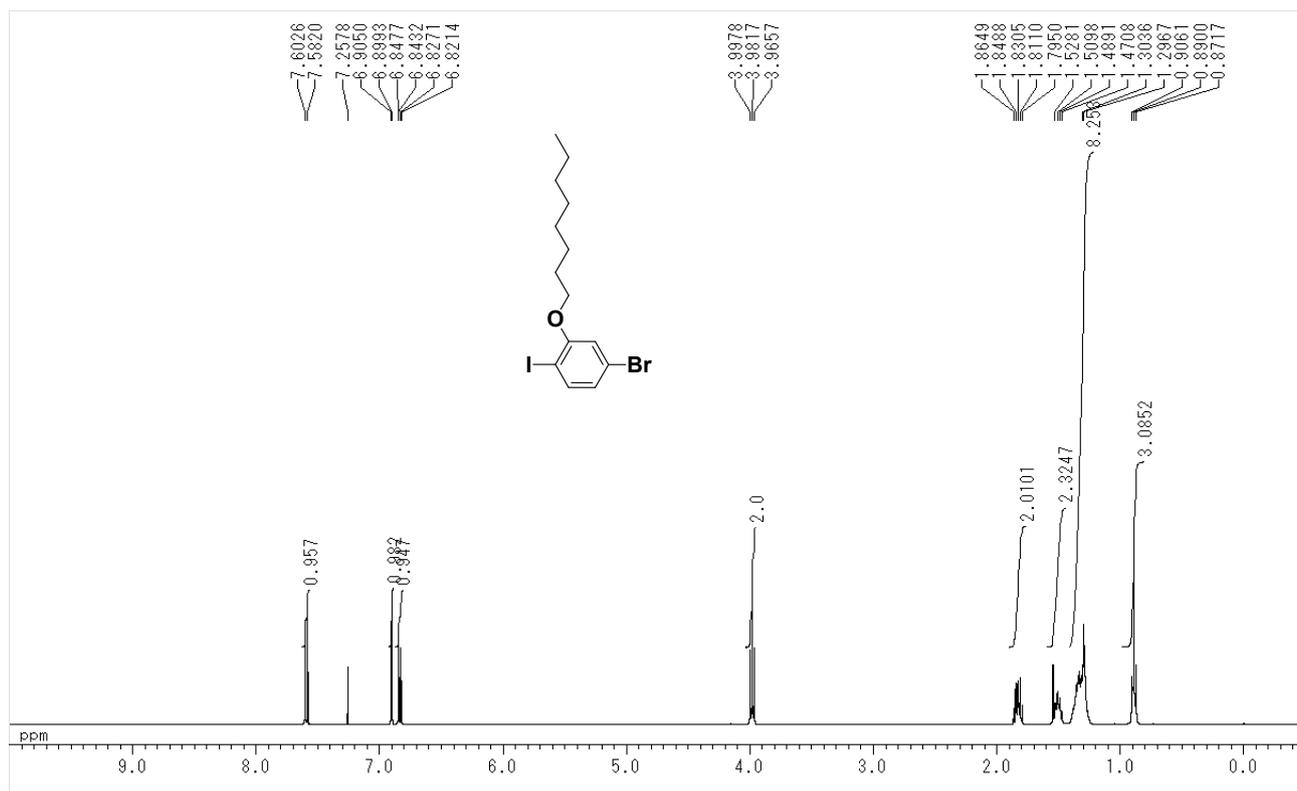
4-Bromo-1-iodo-2-octyloxybenzene (1). In a two-necked flask, 2-fluoro-4-bromiodobenzene (5.0 g, 16.6 mmol), 1-octanol (21.6 g, 165 mmol), potassium tert-butoxide (*t*-BuOK) (2.2 g, 19.6 mmol), and THF (82.9 ml) were mixed with stirring at 80 °C for 2 days. After cooling to room temperature, the reaction mixture was poured into the water and aqueous NH₄Cl was added to a solution. The resultant solution was extracted with diethyl ether. The organic layer was washed with water and dried over anhydrous Na₂SO₄. After removal of the solvents, products were purified by column chromatography on silica gel using a hexane as the eluent, yielding **1** as colourless oil (5.5 g, 81 % yield). ¹H NMR (400 MHz, CDCl₃, δ/ppm) 0.89 (t, *J* = 6.4 Hz, 3H), 1.20-1.40 (m, 8H), 1.47-1.56 (m, 2H), 1.79-1.86 (m, 2H), 3.98 (t, *J* = 6.4 Hz, 2H), 6.84 (dd, *J*₁ = 8.2 Hz, *J*₂ = 1.8 Hz, 1H), 6.89 (d, *J* = 2.2 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, δ/ppm) 14.10, 22.65, 25.99, 28.90, 29.19, 31.77, 69.49, 84.81, 115.40, 122.77, 125.23, 140.01, 158.34.

4-Bromo-2-octyloxyboronic acid (2). In a two-necked flask, a solution of **1** (5.5 g, 13.3 mmol) in dry THF (142 ml) was cooled at -78 °C under an Ar atmosphere. *n*-BuLi (1.65 mol dm⁻³ (M) in hexane, 8.9 ml) was added dropwise to the reaction mixture, which was stirred for 20 min at -78 °C. Triisopropyl borate (B(O*i*Pr)₃) (10.5 ml, 39.9 mmol) was added dropwise to the reaction mixture, which was gradually warmed to room temperature and was stirred overnight. After cooling at 0 °C, 2M aqueous HCl was added dropwise to the resultant mixture, which was stirred for 20 min and was extracted with diethyl ether. The organic layer was washed with brine and water, and dried over anhydrous Na₂SO₄. After removal of the solvents, products were purified by column chromatography on silica gel using a ethyl acetate, dichloromethane and hexane mixture (1:1:2, v:v:v) as the eluent, yielding **2** as a white solid (2.7 g, 61 % yield). ¹H NMR (400 MHz, CDCl₃, δ/ppm) 0.82 (t, *J* = 7.3 Hz, 3H), 1.19-1.31 (m, 8H), 1.35-1.43 (m, 2H), 1.74-1.82 (m, 2H), 3.98 (t, *J* = 6.4 Hz, 2H), 5.63 (s, 1H), 6.97 (d, *J* = 1.4 Hz, 1H), 7.09 (dd, *J*₁ = 6.4 Hz, *J*₂ = 1.4 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, δ/ppm) 14.07, 22.61, 25.97, 29.06, 29.11, 29.21, 31.72, 68.85, 114.54, 124.30, 126.69, 137.88, 164.42.

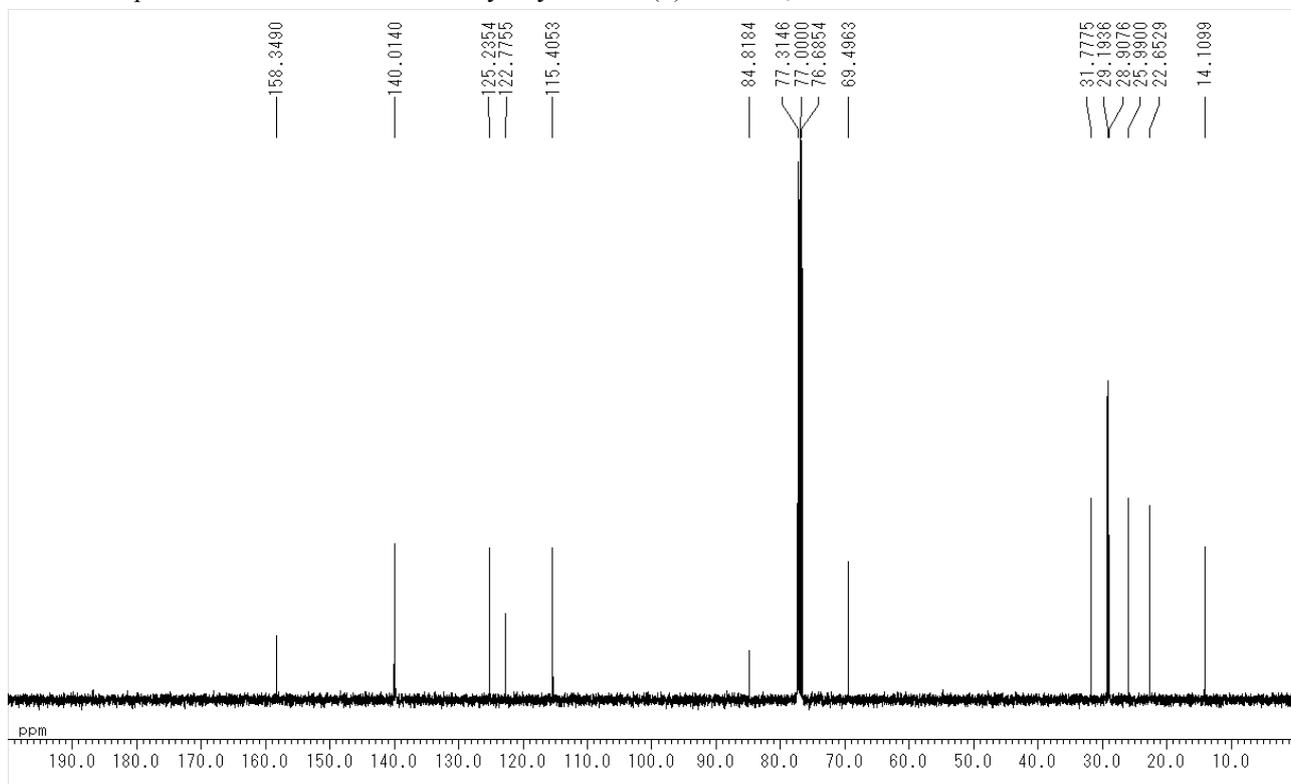
2,7-Dibromo-4-octyloxy-9H-carbazole (4). In a two-necked flask, **2** (448 mg, 1.35 mmol), 2,5-dibromonitrobenzene (379 mg, 1.35 mmol), benzene (1.8 ml), 2M aqueous K₂CO₃ (1.3 ml), and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (7.36 mg) were mixed with stirring at 80 °C for 72 h under an Ar atmosphere. After cooling to room temperature, the resultant solution was extracted with diethyl ether. The organic layer was washed with water, and dried over anhydrous Na₂SO₄. After removal of the solvent, products were purified by column chromatography on silica gel using a hexane and dichloromethane mixture (1:1, v:v) as the eluent, yielding **3** (272 mg) with few by-products. The compound **3** was used without further purification. In a two-necked flask, **3** (272 mg) and triethyl phosphite (P(OEt)₃) (0.9 ml) were mixed with stirring at 155 °C for 48 h under an Ar atmosphere. After cooling to room temperature, P(OEt)₃ was removed, and products were purified by column chromatography on silica gel using a hexane and dichloromethane mixture (1:1, v:v) as the eluent, yielding **4** as a white solid (100 mg, 39 % yield). ¹H NMR (400 MHz, CDCl₃, δ/ppm) 0.89 (t, *J* = 6.8 Hz, 3H), 1.28-1.46 (m, 8H), 1.54-1.61 (m, 2H), 1.93-2.00 (m, 2H), 4.17 (t, *J* = 6.4 Hz, 2H), 6.79 (d, *J* = 1.4 Hz, 1H), 7.17 (d, *J* = 1.4 Hz, 1H), 7.35 (dd, *J*₁ = 8.2 Hz, *J*₂ = 1.8 Hz, 1H), 7.53 (d, *J* = 1.4 Hz, 1H), 8.01 (s, 1H), 8.06 (d, *J* = 8.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, δ/ppm) 14.10, 22.66, 26.14, 29.23, 29.30, 31.79, 68.46, 105.67, 106.54, 111.30, 113.10, 118.65, 120.11, 121.36, 123.36, 123.95, 139.38, 141.11, 155.67. Anal Calcd for C₂₀H₂₃Br₂NO: C, 53.00; H, 5.12; N, 3.09. Found: C, 53.26; H, 5.23; N, 3.04.

2,7-Dibromo-9-(1-octylnonyl)-4-octyloxy-9H-carbazole (5). Potassium hydroxide (KOH) (308 mg), **4** (500 mg, 1.10 mmol), and dimethyl sulfoxide (DMSO) (4.48 ml) were mixed with stirring at 60 °C. A solution of 9-heptadecane *p*-toluenesulfonate (677 mg, 1.65 mmol) in DMSO (2.68 ml) was added dropwise to the reaction mixture, which was stirred overnight. After cooling to room temperature, the reaction mixture was poured into water. The organic layer was washed with water, and dried over anhydrous Na₂SO₄. After removal of the solvents, products were purified by column chromatography on silica gel using a hexane as the eluent, yielding **5** as colourless oil (600 mg, 78 % yield). ¹H NMR (400 MHz, CDCl₃, δ/ppm) 0.81-0.91 (m, 9H), 0.93-1.44 (m, 32H), 1.54-1.62 (m, 2H), 1.83-1.90 (m, 2H), 1.93-2.00 (m, 2H), 2.10-2.25 (m, 2H), 4.17 (t, *J* = 6.8 Hz, 2H), 4.30-4.45 (m, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 61 Hz, 1H), 7.31 (d, *J* = 6.8 Hz, 1H), 7.65 (d, *J* = 63 Hz, 1H), 8.14 (q, *J* = 21 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, δ/ppm) 14.05, 14.10, 22.58, 22.66, 26.18, 26.66, 29.11, 29.23, 29.25, 29.26, 29.31, 31.57, 31.72, 31.79, 33.47, 33.52, 56.88, 57.09, 68.42, 104.76, 104.92, 105.15, 107.46, 110.10, 111.53, 113.87, 118.05, 118.64, 119.47, 119.98, 120.41, 121.90, 122.46, 123.95, 124.16, 138.58, 140.29, 142.09, 143.82, 155.66, 155.81. Anal Calcd for C₃₇H₅₇Br₂NO: C, 64.25; H, 8.31; N, 2.03. Found: C, 64.36; H, 8.22; N, 2.27.

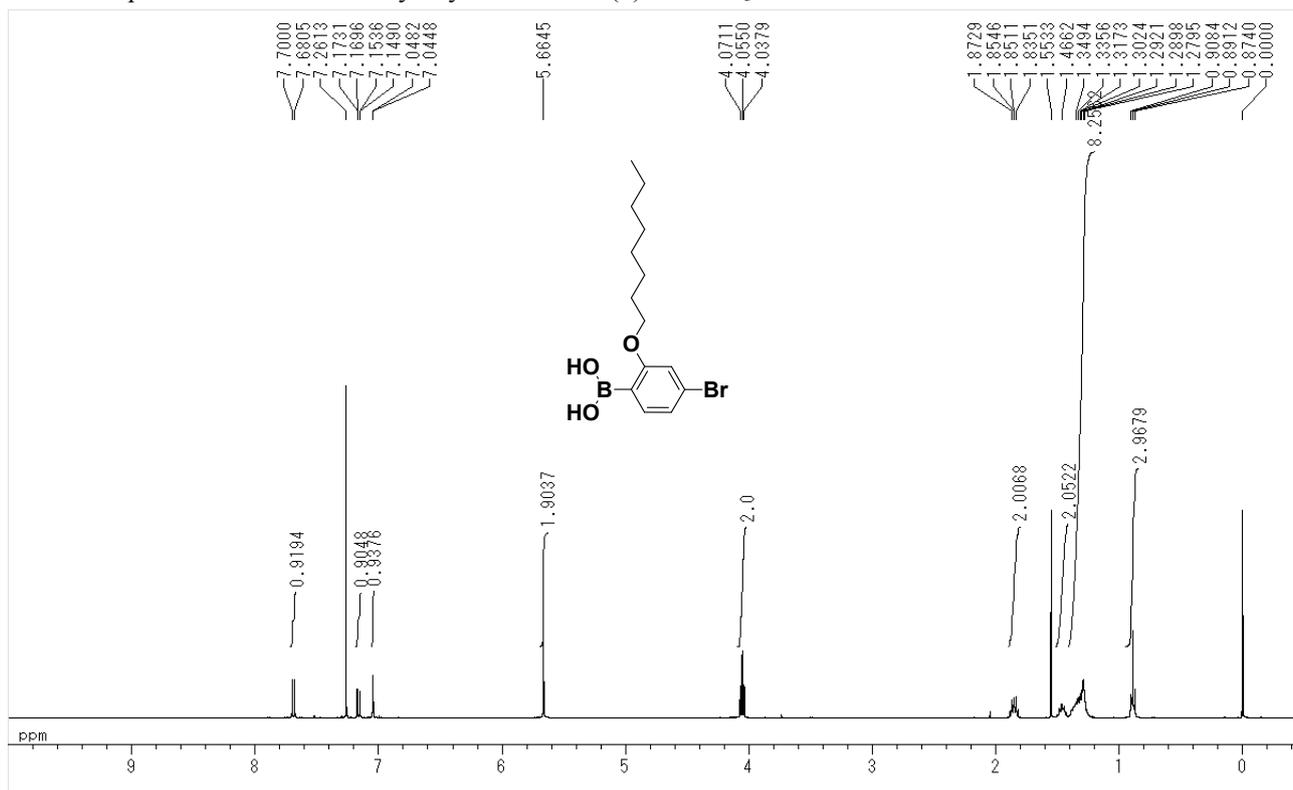
^1H NMR spectra of 4-bromo-1-iodo-2-octyloxybenzene (1) in CDCl_3 400 MHz.



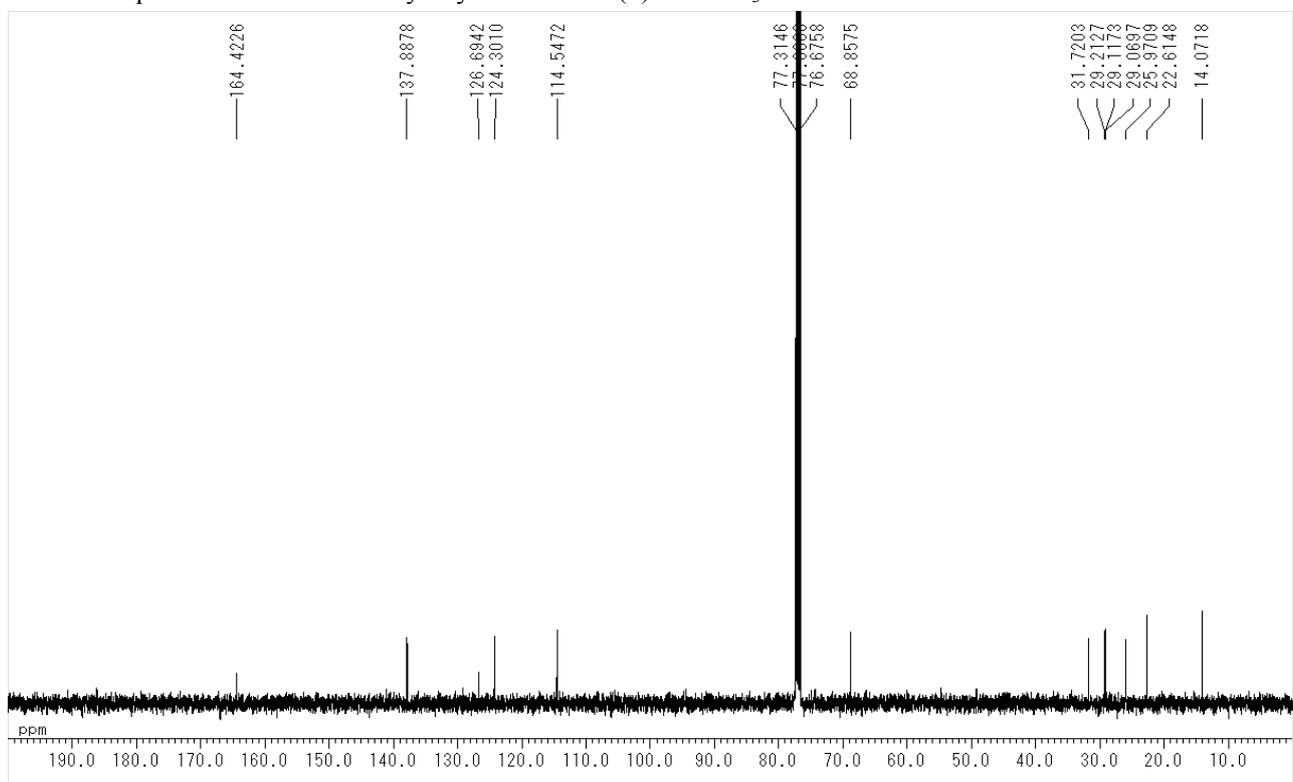
^{13}C NMR spectra of 4-bromo-1-iodo-2-octyloxybenzene (1) in CDCl_3 100 MHz.



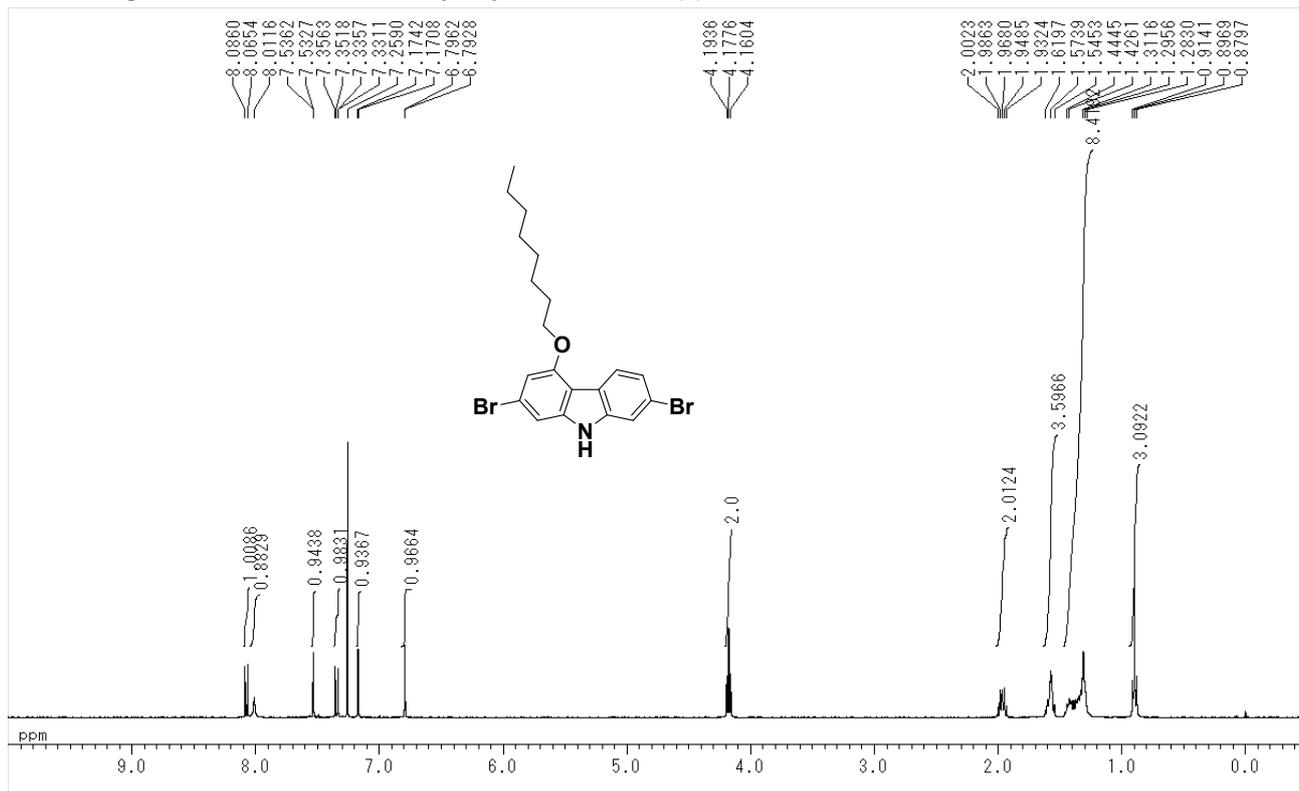
^1H NMR spectra of 4-bromo-2-octyloxyboronic acid (2) in CDCl_3 400 MHz.



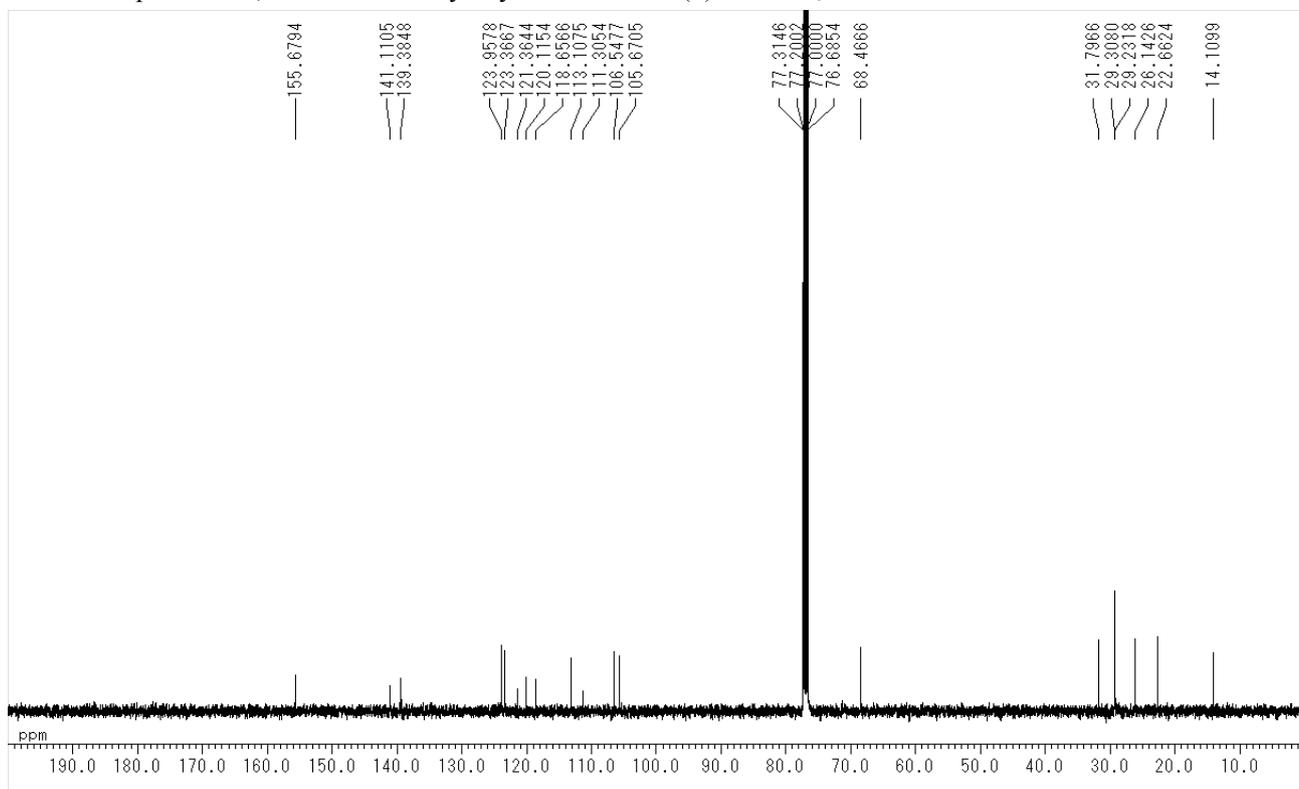
^{13}C NMR spectra of 4-bromo-2-octyloxyboronic acid (2) in CDCl_3 100 MHz.



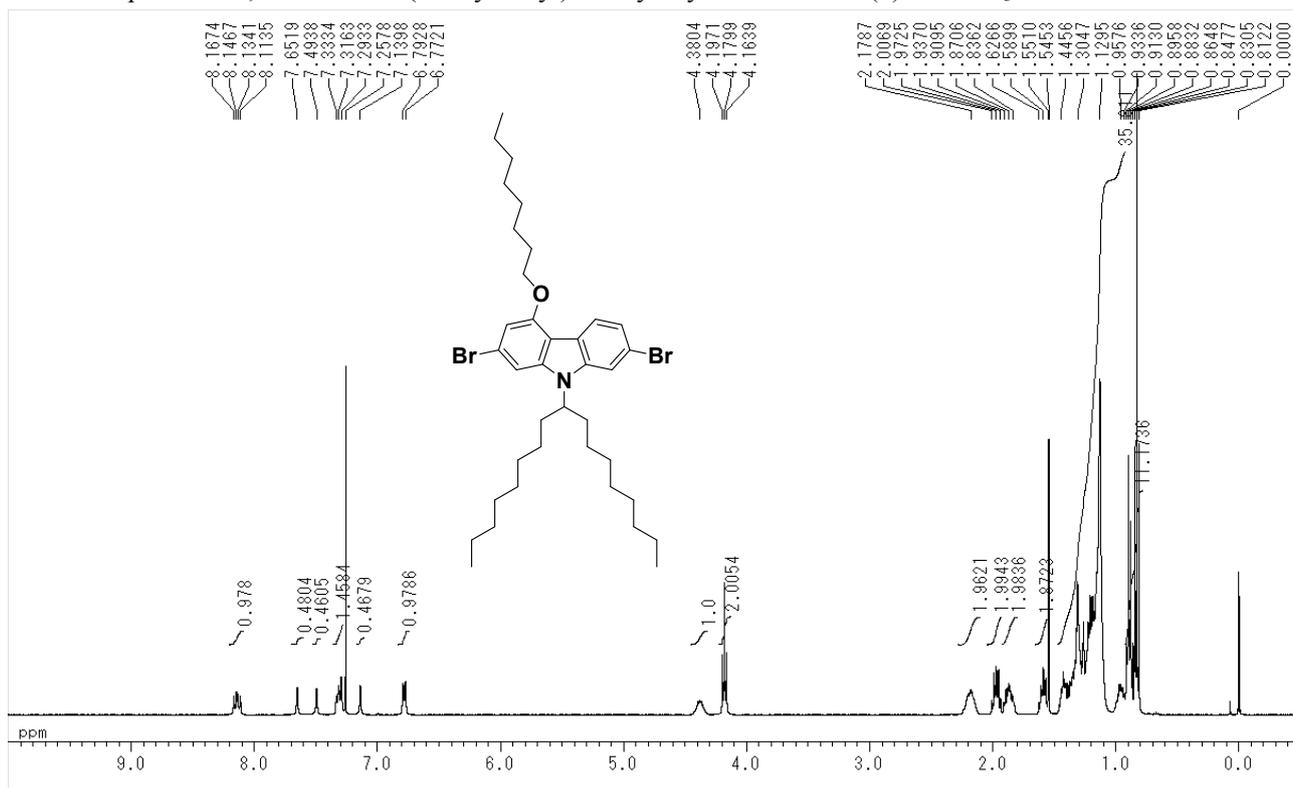
¹H NMR spectra of 2,7-dibromo-4-octyloxy-9H-carbazole (4) in CDCl₃ 400 MHz.



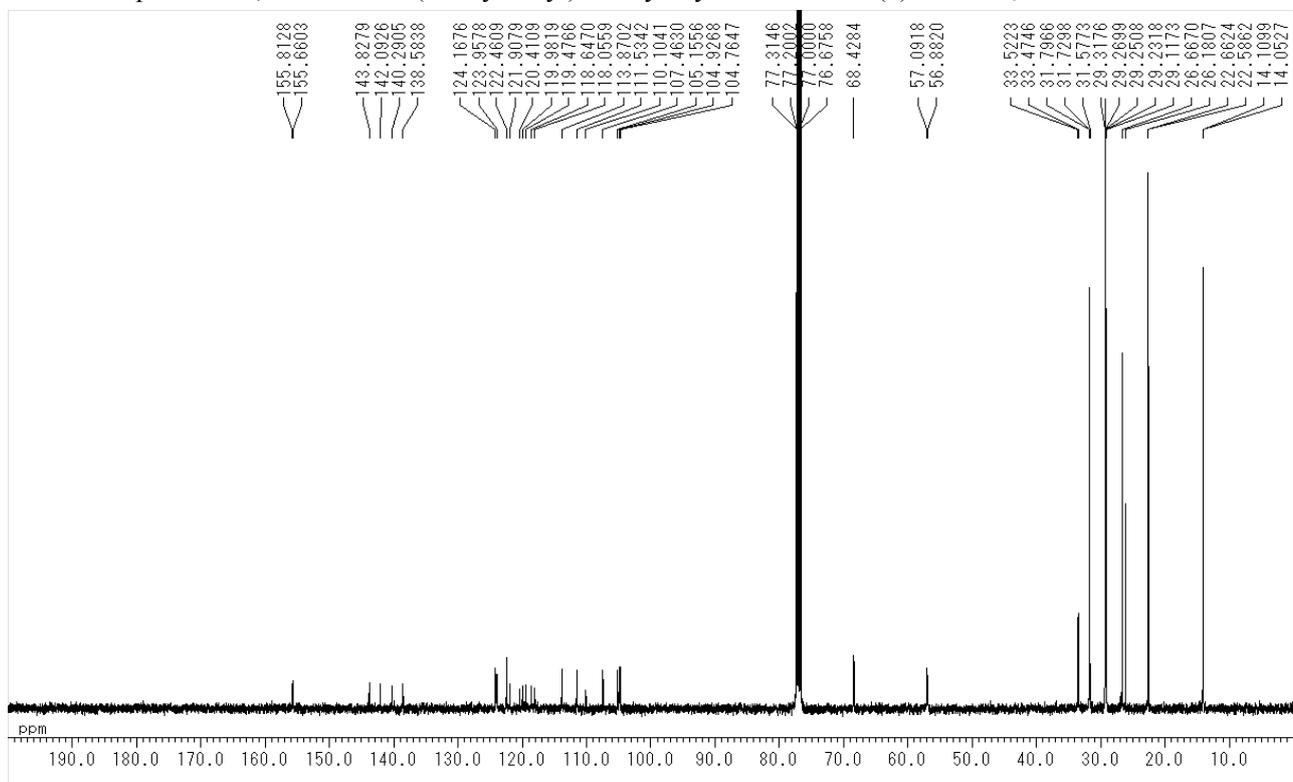
¹³C NMR spectra of 2,7-dibromo-4-octyloxy-9H-carbazole (4) in CDCl₃ 100 MHz.



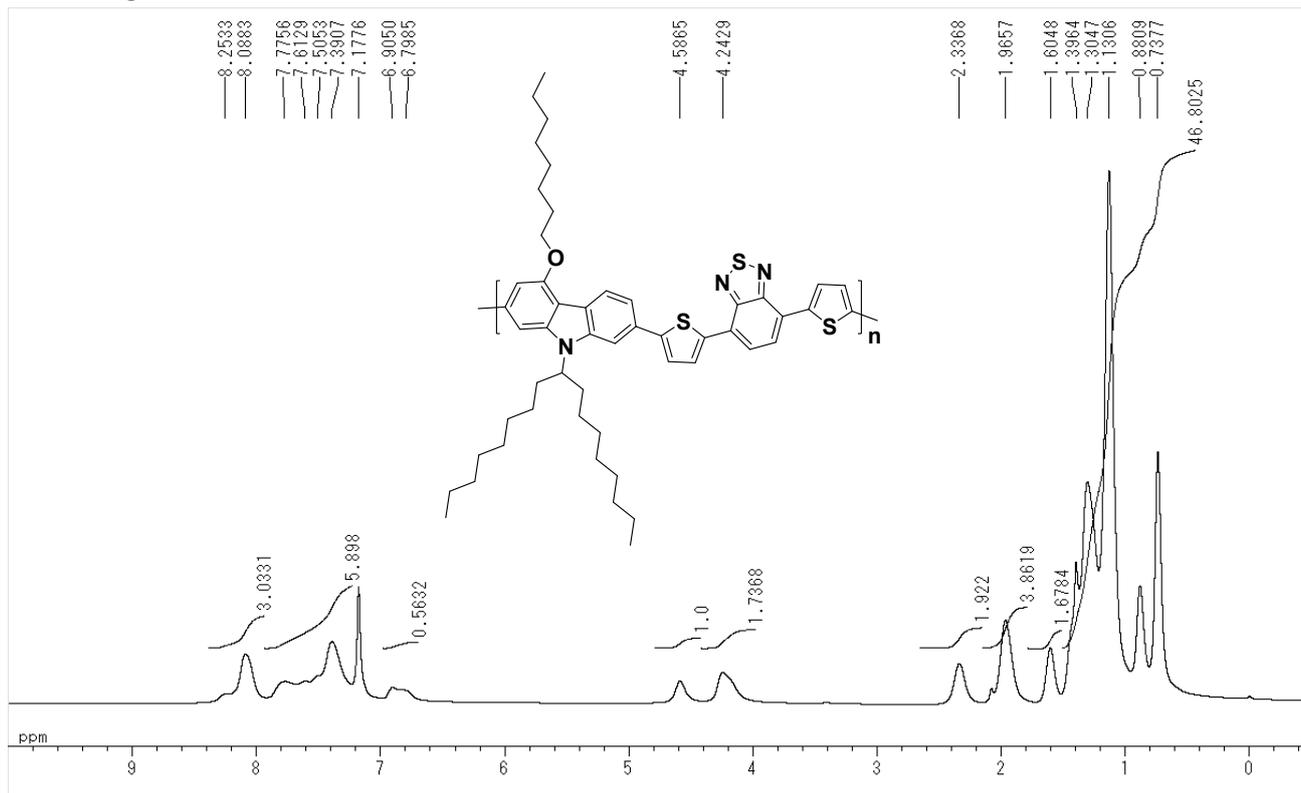
^1H NMR spectra of 2,7-dibromo-9-(1-octylonyl)-4-octyloxy-9H-carbazole (5) in CDCl_3 400 MHz.



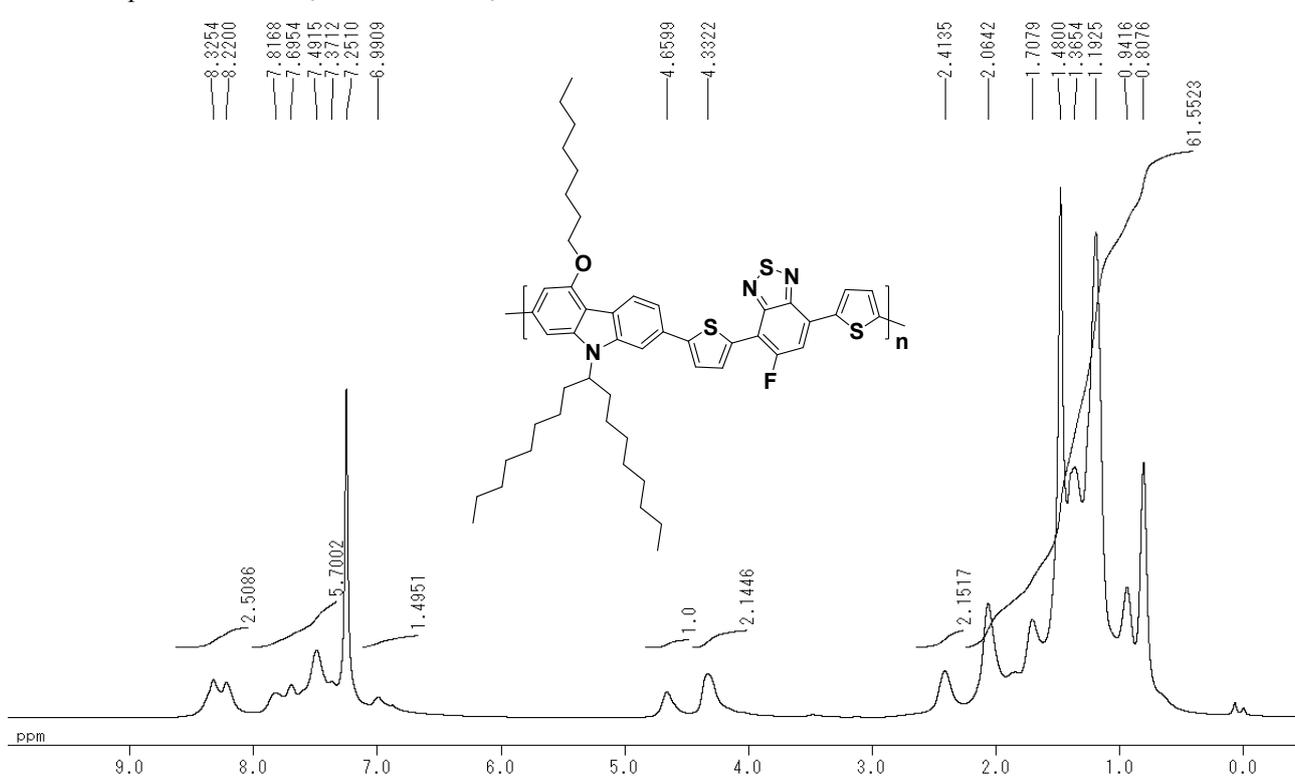
^{13}C NMR spectra of 2,7-dibromo-9-(1-octylonyl)-4-octyloxy-9H-carbazole (5) in CDCl_3 100 MHz.



^1H NMR spectra of PCOC₈-TB in CDCl₃ 400 MHz.



^1H NMR spectra of PCOC₈-TBF₁ in CDCl₃ 400 MHz.



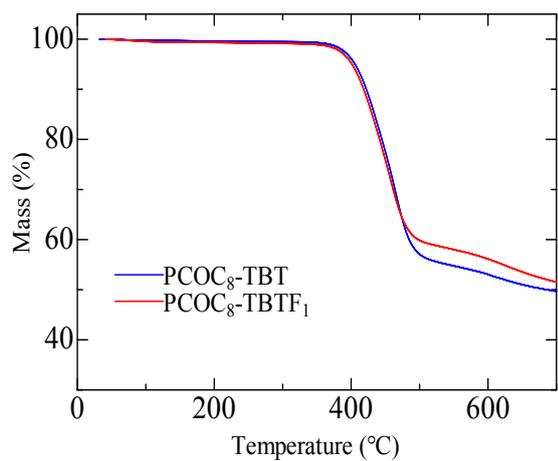


Figure 1S. TGA curves of the polymers.

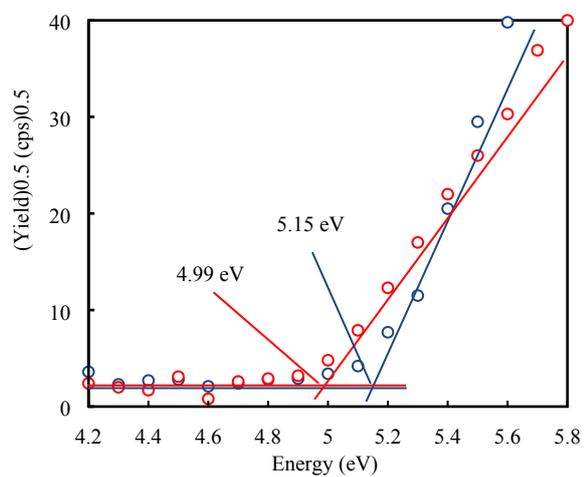


Figure 2S. Photoemission yield spectroscopy of **PCOC₈-TBT** (blue) and **PCOC₈-TBTF₁** (red) in the atmosphere.